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Supplementary Information

Correlating Anisotropy and Disorder with the Surface Structure of Platinum Nanoparticles

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1 Ensemble extraction and Examples

In their raw form trajectories from MD simulations are not suitable for statistical analysis or machine learning, since redundant structures, or those that are statistically indistinguishable based on their energy or coordinate geometries, can result in an over representation of certain types of structures which are an artefact of the simulation. It is important to process the data to extract structures from the trajectory when they become statistically different; simultaneously removing unbound atoms, smaller clusters or particles formed *via* secondary nucleation. An illustration of this extraction, and the type of structures present in the final ensemble, is provided in below, for T=30°C, τ= 0.5 atoms per ns, T=100°C, τ= 0.5 atoms per ns, and for T=100°C, τ= 2 atoms per ns as representative examples.

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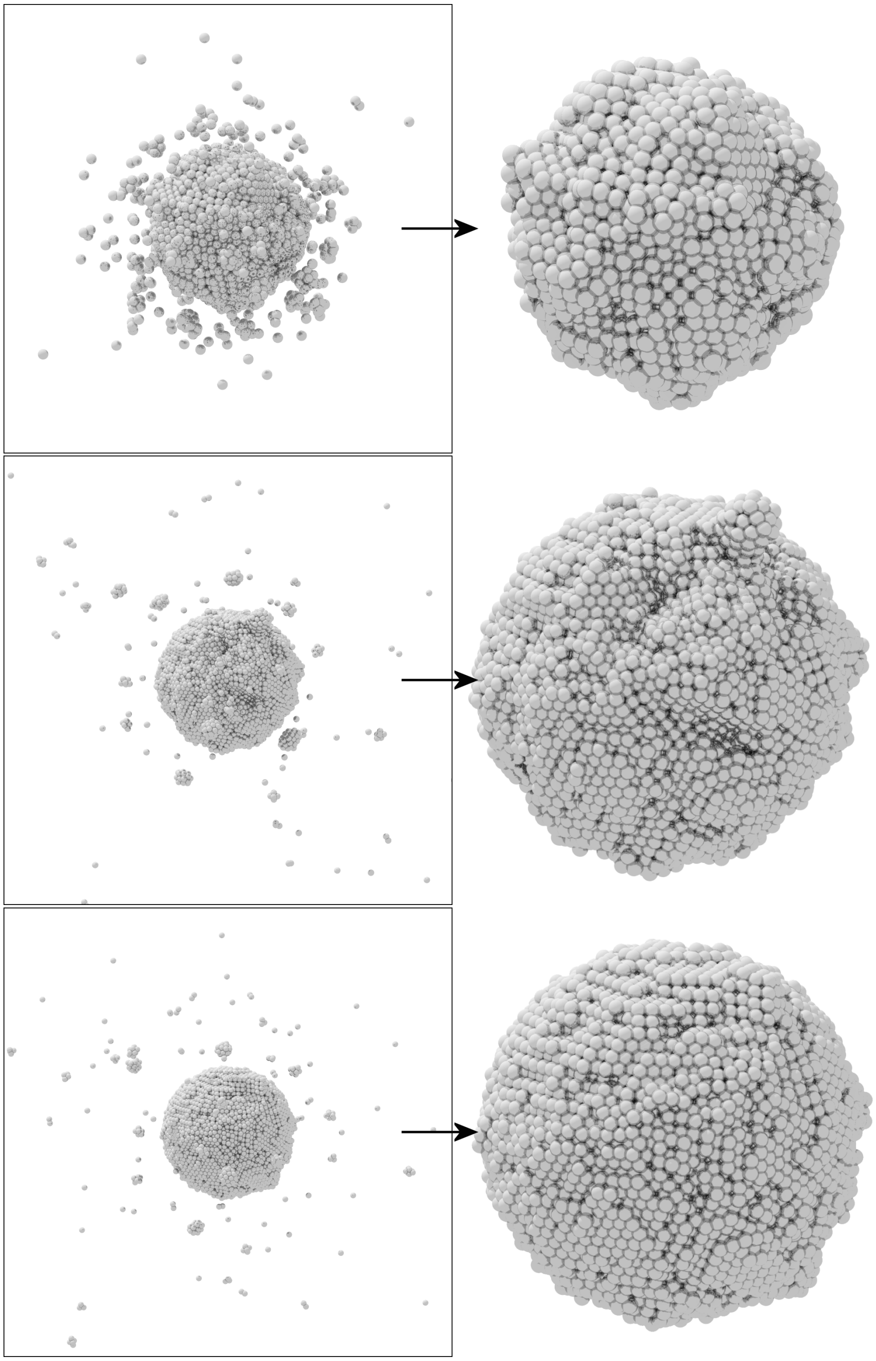
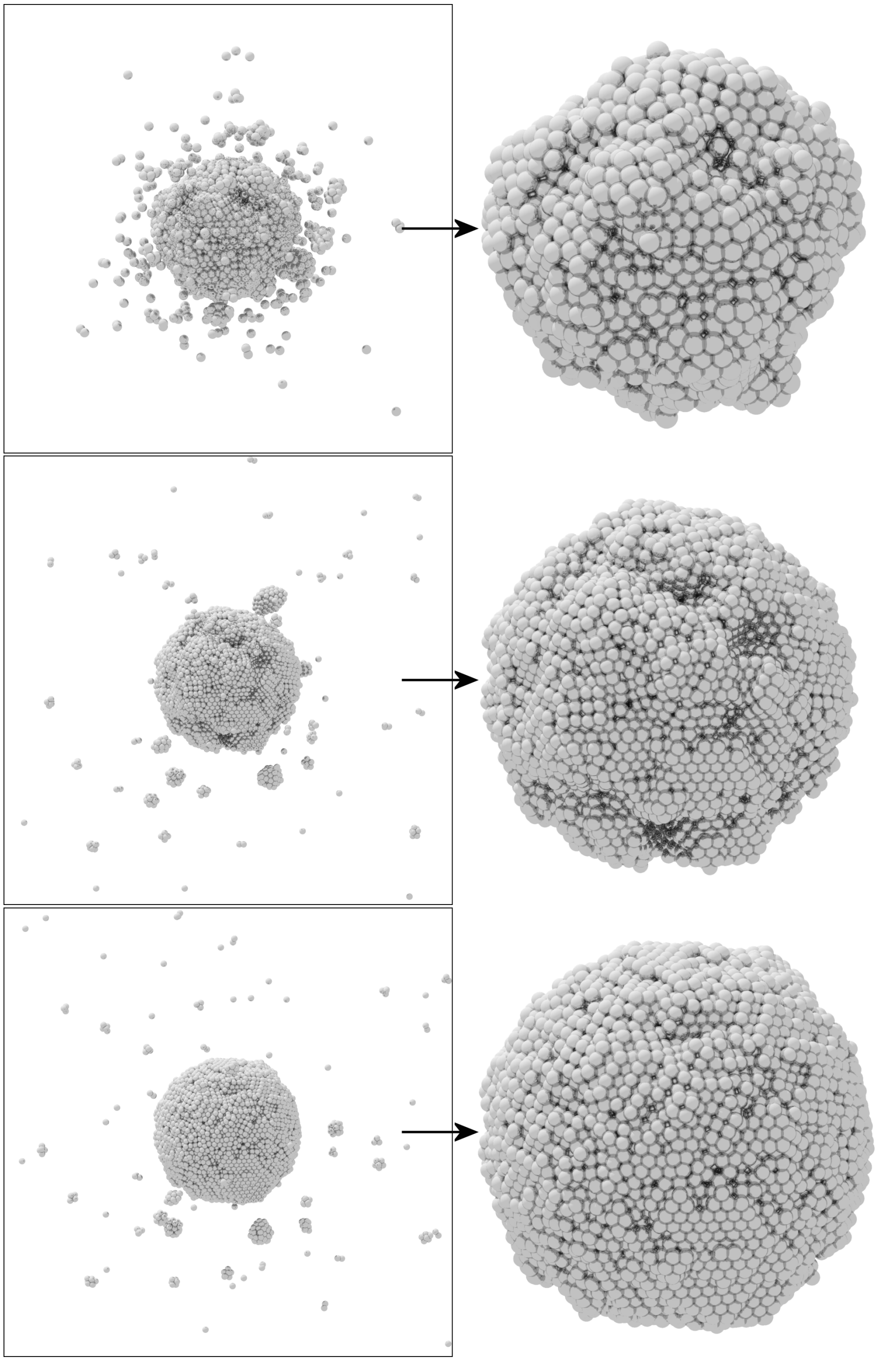
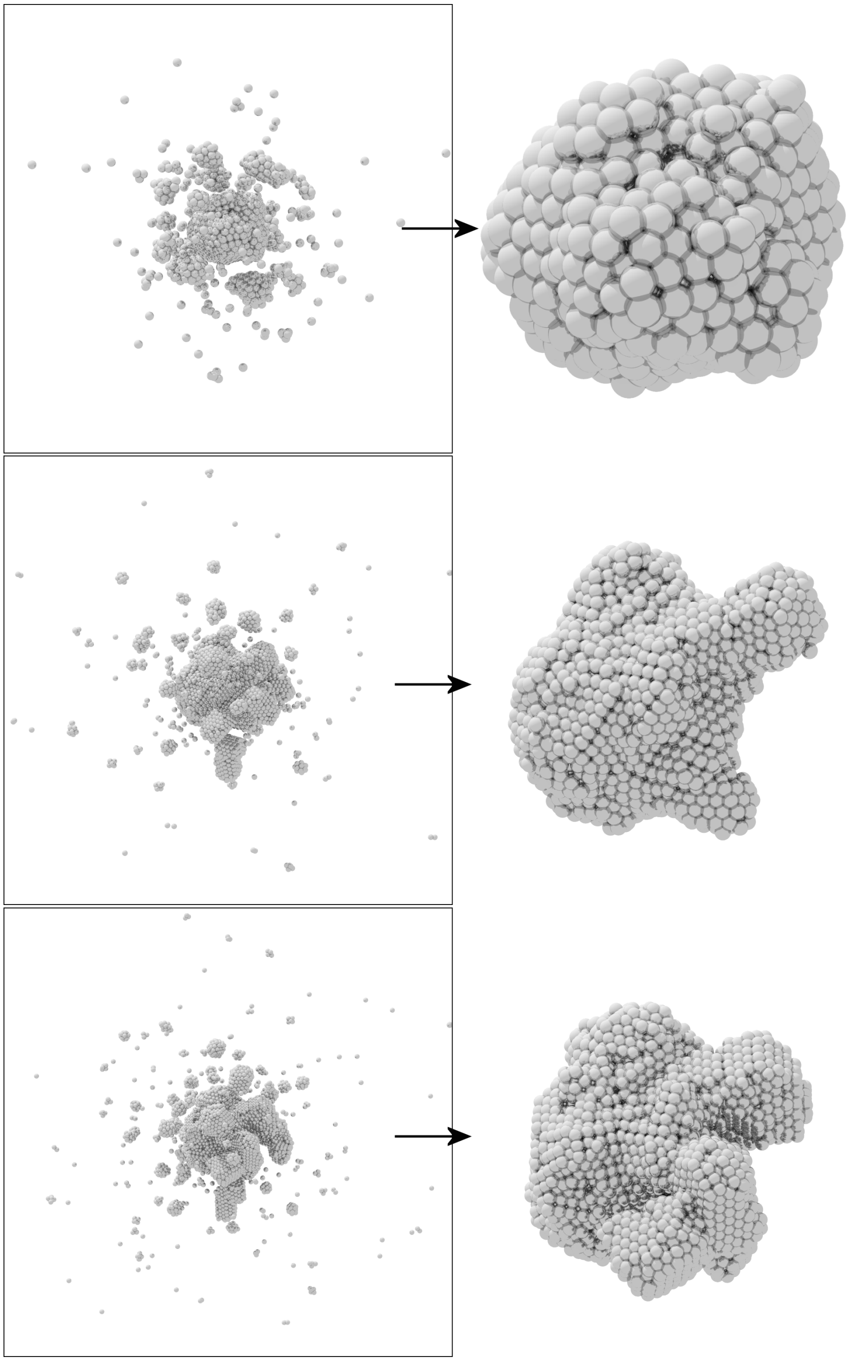


Examples of the type of MD simulation (left) and extracted primary particle (right) present in the ensemble, for T=30°C, τ= 0.7 atoms per ns, at three different points along the MD trajectory.



Examples of the type of MD simulation (left) and extracted primary particle (right) present in the ensemble, for T=100°C, τ= 0.7 atoms per ns, at three different points along the MD trajectory.



Examples of the type of MD simulation (left) and extracted primary particle (right) present in the ensemble, for T=100°C, τ= 2 atoms per ns, at three different points along the MD trajectory.

2 Measures of Order and Disorder

As mentioned in the main text, bulk ordering and classification was performed *via* two methods. Structural analysis and characterization was performed on the surface layer and underlying bulk *via* separate unique methods, as previously shown for gold nanorods[1] and nanoparticles.[2] To determine whether an atom is part of the surface layer, a radial shell of equidistant points is placed around the atom at a radius near the bond distance cut-off (minimum between the first and second peaks in the radial distribution function). At each of these points, a test atom was inserted and checked to see if overlapped any real atoms within the system. If no overlap occurred, the atom was classified as a surface atom; else it was classified as bulk.

General ordering is initially classified by the uses of a previously employed q6q6 bond order parameter scheme.[3] Briefly, for an atom i with neighbours $n(i)$, the local orientational structure is characterized by:

$$\bar{q}_{lm}(i) = \frac{1}{n(i)} \sum_{j=1}^{n(i)} Y_{lm}(\vec{r}_{ij}) \tag{1}$$

where $Y_{lm}(\vec{r}_{ij})$ are the spherical harmonics related to the orientation of vector $\vec{r}_{ij}$ between atom i and its neighbour j. With the restriction to $l = 6$ used traditional to probe hard sphere packing, a vector $\vec{q}_6(i)$ is assigned to each atom with the element $m = -6, \ldots, 6$ given by:

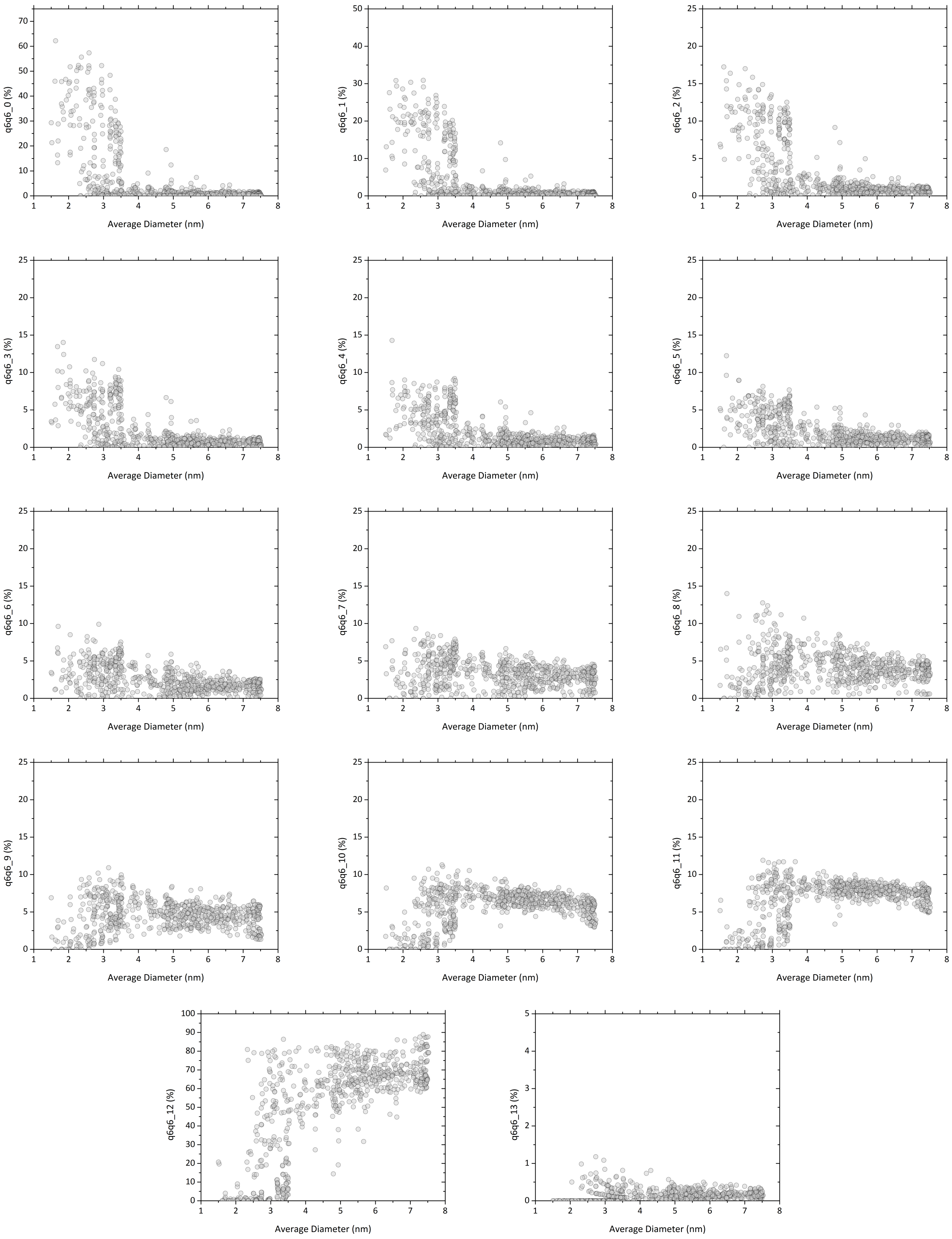
$$q_6(i) = \frac{\bar{q}_{6m}(i)}{\left(\sum_{m=-6}^{6} |\bar{q}_{6m}(i)|\right)^{1/2}} \tag{2}$$

where the looping is over the first nearest neighbours defined by a cutoff distance generally found by looking for the minimum between the first and second peak in the radial distribution function (3.4Å used in this work). A quantitative comparison of the similarity in the orientational bonding environments between two atoms can be achieved via the dot product $\vec{q}_6(i) \cdot \vec{q}_6(j)$. We define the similarity coordination $n_s(i)$ of atom i as the sum of all first nearest neighbours that have a value of this dot product exceeding 0.7. Highly ordered regions tend to have values of $n_s(i) > 10$ and can represented close crystalline packing.

For the most highly order regions ($n_s(i) > 10$) ring analysis of the first nearest neighbour bonding network,[4,5] is used to classify the local atomic environment into face-centred cubic (FCC), hexagonal close packed (HCP), icosahedral (ICOS), decahedral (DECA) other ordered structures (ORD). In cases where the atoms do not conform to one of these local atomic environments, we have classified the structure as disordered (DIS), in the context of a platinum lattice. It has been previously shown that these packing environment tend to arise within regions of high similarity coordination.[3] In Figures 2(a), 2(b) and 2(c) in the main text we can see the fraction of different lattice structure present in each particle: FCC, HCP and DIS, respectively. Note that the other bulk structures are not shown, as the majority of particles contained no ICOS, DECA or ORD lattice sites, or the fraction was statistically insignificant. Similar results for all of the original q6q6 parameters are provided here.

In the case of the surface order and disorder the surface curvature and packing was classified separately based on the surface coordination and angles of the surface atomic layer. The surface curvature for each surface atom is calculated from the displacement vectors with its first nearest neighbours. Considering an atom i of coordination 4, with its nearest neighbours as shown below in a near planar configuration. There exists four angles when we loop in a clock-wise or counter clock-wise direction, and the three atoms defining those angles also define four planes. The surface normal to each plane are obtained by the cross product of vectors $\vec{ij}$ and $\vec{ik}$.

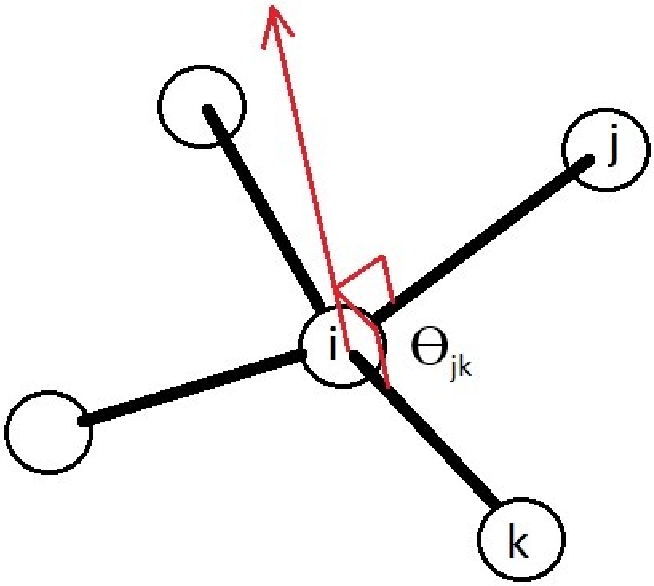
The calculation of an atoms curvature angle uses the four surface normal vectors and determines the average surface normal vector shown in red, along with the average angle between this average vector and the four surface normal vectors. Thus, a planar configuration would give a result of zero. Bases on the coordination of the atoms, their bond angles, and their non-planar curvature, the classification of surface packing can then be defined as shown in the table below. Results for these surface packing structures are presented Figures 2(d), 2(e) and 2(f) in the main text, and similar results for the individual curvatures are provided here; along with more detailed classifications related to different types of catalytic reactions[6] (as described in the main text).



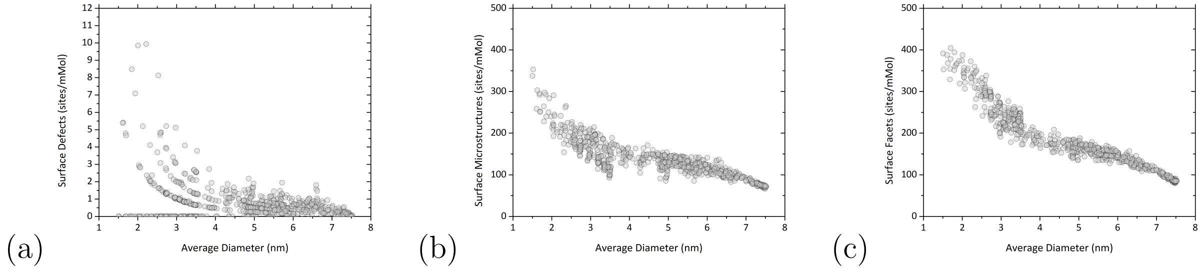
Size-dependent distribution of the q6q6 order parameter for all the nanoparticles in the ensemble.

Table 1: The classification definitions of (100), (111), (110) surface packing environment around an atom.

{hkl}	Curvature (Deg.)	Angle (Deg.)	Coordination
{100}	< 15	$70 < \Theta < 110$	4
{111}	< 15	$40 < \Theta < 80$	6
{110}	> 15	$40 < \Theta < 80$	6

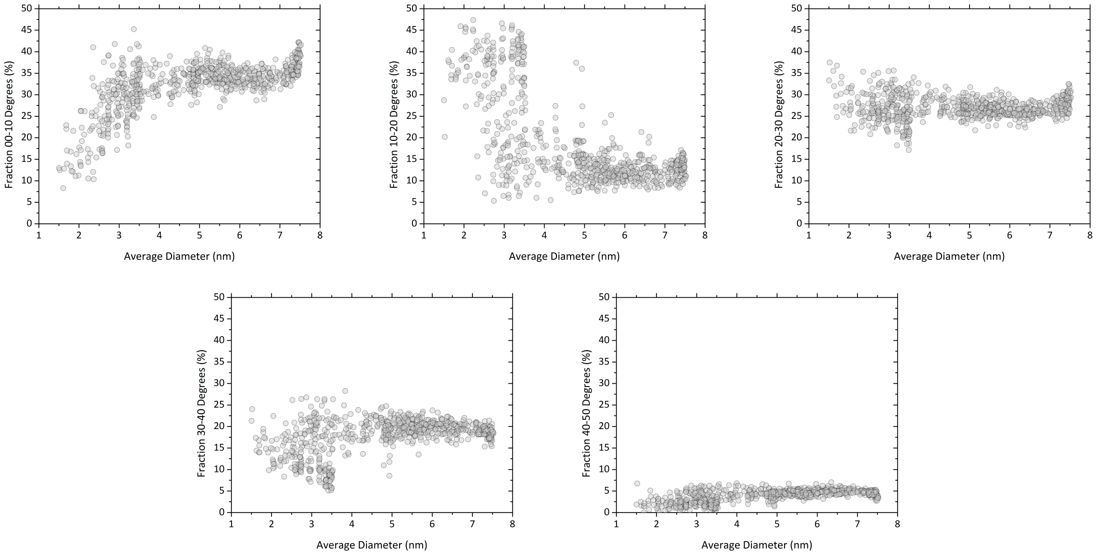


Atom with its first nearest neighbours.

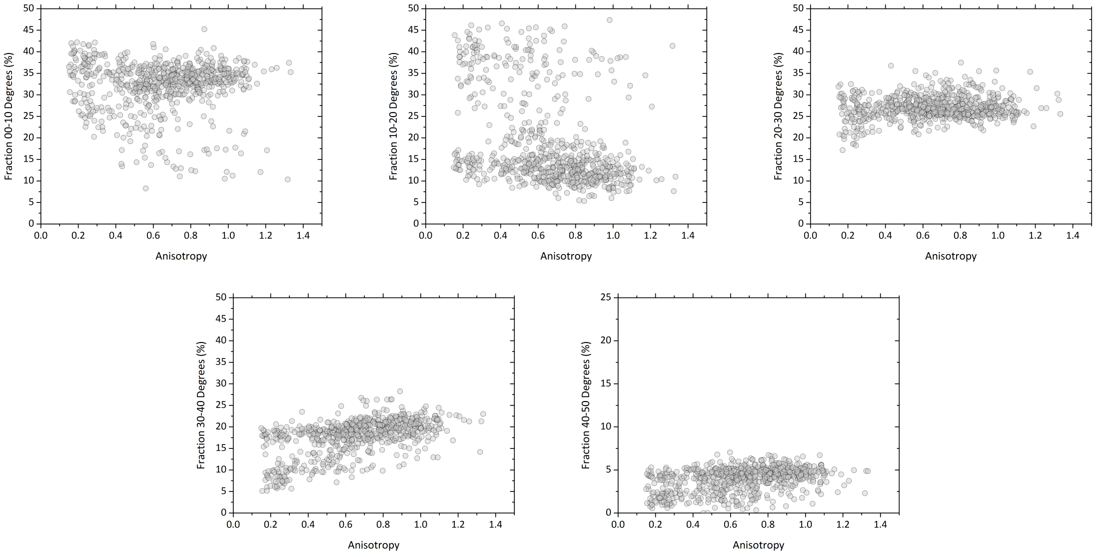


(a) (b) (c)

The mixture of different bulk and surface structures present in each particle in the data set: (a) Surface Defects (SCN 1, 2 or 3), (b) Surface Microstructures (SCN 4, 5, 6 or 7) and (c) Surface Facets (SCN 8, 9, 10 or 11).



Size-dependent distribution of the degree of different surface curvatures.



Anisotropy-dependent distribution of the degree of different surface curvatures.

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